5. Predictive Modeling

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Section Contents

Thermally Enhanced Removal of Liquid Hydrocarbon Contaminants from Soils and Ground Water

Contents

THERMALLY ENHANCED REMOVAL OF LIQUID HYDROCARBON CONTAMINANTS FROM SOILS AND GROUND WATER*

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Abstract

The acceleration of recovery rates of second phase liquid contaminants from the subsurface during gas or water pumping operations is realized by increasing the soil and ground water temperature. Several methods of delivery of thermal energy to soils and ground water are possible. Of these thermal methods, combined steam injection and vacuum extraction appears to be the most economical and versatile technique to recover volatile, semi-volatile, and non-volatile contaminants from the subsurface. One-dimensional experiments have shown effective removal of both volatile and semi-volatile second liquid phase chemicals, as well as non-volatile aqueous phase contaminants from sand packs. Two-dimensional experiments with homogeneous and layered sand packs have shown rapid recovery of volatile and semi-volatile hydrocarbon liquids. The enhancement of mass transfer from lower permeability regions during the de-pressurization mode of operation has been observed to be effective in the removal of residual contaminants. Field scale studies of steam injection and vacuum extraction confirm the effectiveness of this technique and its applicability to contaminants found both above and below the water table.

Introduction

The *in situ* recovery of contaminants from soils is required in many locations where spills have occurred. For volatile contaminants in the unsaturated zone, soil venting has obvious application due to the low viscosity of the carrier fluid (air) and the low capital requirements for implementation. In addition, the high molecular diffusivity of most of the volatile chemicals in air allows successful operation in real geologic environments where mass transfer limitations are certain to occur. However, for low volatility contaminants or for regions below the water table, air venting will not be effective. Beneath the water-table, ground-water pumping has been used extensively. However, cleanup rates with pumping have been found to be slow; particularly in the later stages of cleanup when the dissolution rates become mass transfer limited. In such a situation, the recovery rates are proportional to the aqueous phase diffusivities of the contaminants, which are typically quite small.

The use of thermal techniques to enhance recovery rates of *in situ* "pump-and-treat" operations is of major interest due to the enhanced mass transfer rates that can be obtained. Higher recovery rates mean shorter treatment times and lower volumes of fluid that would be produced and treated. In most remediation projects, the contaminant will consist of many chemical components of varying thermodynamic properties contained in both the high and low permeability zones within the saturated and unsaturated zones. Inevitably, during gas venting operations, the rate of evaporation of the contaminant into the vented air will be mass transfer limited. As such, the evaporation rate of each component will be proportional to its gaseous phase concentration at equilibrium with the multi-component liquid. This concentration is proportional to the vapor

pressure multiplied by the constituent molecular weight, adjusted for its molar fraction in the multi-component liquid. By Raoult's law, this adjustment factor is equal to the component's molar fraction for ideal mixtures. By increasing the temperature from ambient conditions to a higher temperature, significant increases in the vapor pressures and evaporation rates of the contaminants will be realized. Figure 1 shows the equilibrium concentration of several contaminants in air at atmospheric pressure as a function of temperature. The increase in evaporation rate that can be realized by increasing temperature is simply the ratio of the concentration at 100 °C to that at 20 °C for equal vapor flow rates and subsurface fluid flow distributions. For the compounds shown in Figure 1, these ratios are from 25 to 40. The concentration ratios are inversely proportional to the remediation time-scale. For compounds with boiling points greater than that of the water at near atmospheric pressure, complete vaporization of a liquid phase contaminant can occur with reasonable energy cost. Semi-volatile compounds are particularly amenable to thermally enhanced extraction due to the large change in vapor pressure with temperature. Furthermore, for longer chained "non-volatile" components such as naphthalene, evaporation can occur at significant rates only if the temperature is increased. However, for low volatility petroleum hydrocarbons such as diesel or lubricating oils, vaporization rates will be limited by low vapor pressures even with thermal enhancement.

In situ thermal techniques include electrical heating, radio frequency heating, hot air injection, hot water injection, and steam injection. Electrical heating and radio frequency heating would typically be used in conjunction with either soil-gas or ground water pumping. The increase in vapor pressure and molecular diffusivities with temperature would be exploited to increase the contaminant recovery rates. Since the thermal energy is supplied to the subsurface without the injection of fluids when radio frequency or joule heating is applied, heating occurs preferentially in zones having the highest radio frequency absorptivity or electrical conductivity, respectively. Therefore, they are well suited to low permeability soils. Hot gas injection would have application to the enhancement of recovery rates of semi-volatile contaminants in the unsaturated zone, and

possibly below the water-table. However, the low specific heat of air does not allow high energy input rates unless the gas is very hot. For example, for equivalent mass injection rates, air would need to be injected at over 2200 °C to equal the energy input of steam at 100°C. Hot water injection may find application to the acceleration of the cleanup of contaminants below the water-table due to the trends of decreasing adsorption, decreasing interfacial tension, decreasing density, and increasing solubilities with increasing temperature. But the inherently slow aqueous phase transport processes plaguing cleanup by ground water pumping will still limit the rates.

Combined steam injection and fluid extraction is applicable to the *in situ* cleanup of the subsurface contaminants found above or below the water-table. Steam effectively heats and displaces water from the medium to high permeability zones. Low permeability zones can be effectively heated by thermal conduction if they are surrounded by steam bearing regions. This range of applicability is the motivation for the interest this process has received during the last few years. As with other thermal techniques, significant gains in the rates of contaminant recovery can be realized by the heating of the soil to steam temperatures. But the injection of steam is unique in that it provides for the dilution and displacement of nonvolatile contaminants from regions below the water-table, effective dewatering of contaminant laden strata providing additional contaminant-steam contact, and enhanced mass transfer from the low permeability zones during de-pressurization. The last mechanism, while thermodynamically subtle, will have dramatic influence on the recovery of contaminants from heterogeneous environments including fractured media. The use of steam injection to exploit these mechanisms constitutes the use of the steam enhanced extraction process (Udell, *et al*, 1991) discussed herein.

The use of thermal techniques for the recovery of volatile and semi-volatile liquids from porous media is not new. A large body of research on steam injection for enhanced oil recovery by viscosity reduction and distillation can be found in the petroleum literature (i.e., Mandl and Volek, 1969, Volek and Pryor, 1972, and Konopnicki et al., 1979). However, the use of thermal

processes for the in situ recovery of contaminants has a very short history. Early exploratory field work on steam injection was carried out in the Netherlands in the early 1980's (Hilberts, 1985). Radio frequency heating has been tested (Dev, 1986) as has *in situ* vitrification by resistance heating (Fitzpatrick et al., 1986). More recently, combined steam injection and vacuum recovery for solvent recovery was pilot tested by Udell and Stewart (1989). A field-scale cleanup of a diesel spill followed (Van Sickle, 1992). The process was applied to the full-scale cleanup of a gasoline spill at Lawrence Livermore National Laboratory (LLNL) in 1993. Summary results of the LLNL project are presented in this work.

More definitive laboratory experiments on steam injection for volatile and semi-volatile liquid contaminant recovery have been reported. Lord et al. (1987) reported kerosene removal efficiencies as functions of time of steam contact and soil type. Hunt, Sitar and Udell (1988) reported removal of pure trichloroethene, a mixture of benzene and toluene, and gasoline as separate liquid phases flowing ahead of the steam condensation front. Stewart and Udell (1988) developed three phase flow solutions to the problem of steam displacement of volatile and non-volatile liquid contaminants and verified the theory with experimental data. Yuan (1991) and Yuan and Udell (1993) showed the conditions necessary to build a bank of separate phase liquid ahead of the steam condensation front based on criteria related to the vapor pressure of the contaminant components.

In addition to a presentation of the more relevant information found in the literature, new data obtained from laboratory and field research is reported herein. In the following sections, data and discussion are presented first in a one-dimensional context. Results of two-dimensional visualization experiments are then reported. Finally, the results of two field demonstrations will be presented and discussed. The data are used to illustrate the dominant mechanisms that are exploited in the use of combined steam injection and vacuum extraction for the cleanup of soil and ground water contaminated by second liquid phase contaminants.

One Dimensional Studies

A series of one dimensional studies have been completed including the steam displacement of TCE, a benzene-toluene mixture, and gasoline with essentially complete recovery and separate phase hydrocarbon recovery immediately ahead of the steam condensation front (Hunt, Sitar and Udell, 1988). Stewart and Udell (1988) reported experimental data showing that low volatility mineral oil is not displaced by steam, although evidence of steam distillation in the steamed region was found. This result was consistent with the data of Lord et al. (1988) showing recovery of kerosene in the effluent steam. Yuan (1991) and Yuan and Udell (1993) showed that for contaminant components with vapor pressure greater than that of decane at steam temperatures, a bank of separate phase liquid may develop ahead of the steam condensation front. Vaughan, Udell and Wilts (1993) examined salt displacement by steam injection using electrical conductivity measurements to gain spatial information on salt concentrations ahead of the steam condensation front. These experimental and theoretical studies provided a great deal of insight into the mechanisms governing the removal of volatile, semi-volatile, and non-volatile contaminants from porous media. The dominant mechanisms are detailed and illustrated in the following sections.

Displacement of Aqueous Phase and Non-Aqueous Phase Contaminants

A simple one-dimensional conceptual model aids the understanding of the unique characteristics of steam injection. When saturated steam is injected into an initially cool porous medium, the steam condenses, giving up the latent heat of vaporization to heat the porous solid and interstitial fluids. With continued injection, three distinct zones will develop as illustrated in Figure 2: a nearly isothermal steam zone, a variable temperature zone, and an isothermal zone at the ambient medium temperature. Under adiabatic conditions, the rate of expansion of the steam zone is directly proportional to the injected steam enthalpy flux if the length of the variable temperature zone

remains constant with time (Hunt, Sitar and Udell, 1988, and Stewart and Udell, 1988). The interface between the steam zone and the variable temperature zone is essentially the location of the steam condensation front if the temperature gradient in the steam zone is not significant. For injection pressures near atmospheric and soil thermal properties and temperatures characteristic of field conditions, approximately 350 pore volumes of steam will be required to condense to expand the steam zone an additional unit volume. Thus, steam injection is characterized by large vapor flow rates and pressure gradients in addition to high temperatures.

The displacement of the original fluids by the propagation of the steam condensation front is due to the high steam pressure gradients. These high gradients are sufficient to reduce the water saturation to its residual value in distances of less than a meter (Menegus and Udell, 1985) and provide the force necessary to overcome the capillary forces trapping the hydrocarbon phase (Stewart and Udell, 1988). As compared to the injection of a non-condensing gas into a liquid saturated porous medium, hydrodynamic fingering does not occur due to the requirement of over 300 pore volumes of steam to provide the thermal energy to propagate the steam zone into each additional volume of media. Thus, higher pressure gradients are observed in the displacing phase (steam) than in the displaced phases (water and hydrocarbon liquid). Saffman and Taylor (1960) used this condition to define stable displacement. Additional stability of the condensation front has also been attributed to the heat losses from incipient fingers (Stewart and Udell, 1989, Choke, 1975). These stabilizing mechanisms do no prevent larger scale channeling in heterogeneous media however. Rather than the pore-scale fingering that would be observed if gas were injected into a water saturated porous media, only meter scale steam channels are expected during steam injection (Basel and Udell, 1991).

The combination of effective steam displacement of liquid water and the addition of steam condensate at the condensation front produces an unexpected bonus: removal of nearly all aqueous phase solute. Large reductions in aqueous phase solute concentrations due to steam displacement

and dilution has been quantified in a series of one dimensional experiments. The solute chosen was sodium chloride because of its low adsorption on quartz and non-volatility. In an initial series of experiments, a dilute saline solution of 14.0 g/kg concentration was injected into a sand pack until the effluent fluid electrical resistivity matched that of the injected fluid. The 5.04-cm diameter sand pack was then subjected to a steady steam flow rate of 2 gm/min. As the steam condensation front moved steadily through the sand-pack, the effluent was collected in a graduated cylinder. To maintain one-dimensional conditions in the sand pack, a series of heater tapes were sequentially turned on and adjusted in accordance with a predetermined calibration of heat loss versus sand pack/room temperature difference. After steam was observed in the outlet tubing, noted as time of steam breakthrough, injection continued until the effluent mass flux equaled the steam injection rate. The water remaining in the sand pack was thus considered to be immobile and at the irreducible saturation, which was determined from a mass balance to be 12.9%. A measured volume of distilled water was then injected into the steam zone as the column was allowed to cool. At the end of this procedure, the sand pack was completely saturated with water. The system was allowed to rest for 48 hours, allowing the salt remaining in the sand pack to diffuse into the injected water. The water was then allowed to drain from the sand pack through the injection port by gravity. All effluent solutes were analyzed for salt concentrations by atomic adsorption spectroscopy.

Of the 10.1 grams of salt initially in solution in the 0.724 liters of initial pore water, 9.8 grams were recovered in the 0.803 liters of effluent water at the time of breakthrough. An additional 0.0133 grams of salt were removed after breakthrough accounting for the remaining mobile water which flowed from the sand pack from the steam zone. From the measured volumes and salt concentrations of the drained water recovered after the water-flood and resting period, a total salt mass of 0.177 grams was determined to have remained in the sand pack after steam injection. Therefore, while 87.1% of the saline water was displaced by the steam, a decrease in salt concentration of 98.5% was observed as would be calculated on a dry sand mass basis. Thus, the

residual water remaining in the steam zone was diluted on average by a factor of 7.3. Subsequent experiments reported by Vaughan, Udell and Wilts (1993) show similar behavior. Through electrical conductivity measurements, a dilution of the salt concentration of the immobile water remaining in the steam zone by a factor of 10 gave reasonable agreement with measured electrical conductivities of the partially saturated sand. While the economics of using steam displacement to recover non-volatile, aqueous phase contaminants from the subsurface are questionable, this displacement mechanism may be exploited in cleanup operations targeting mixed waste sites.

Distillation in the Steam Zone

Depending on the volatility of a liquid-phase contaminant, it will either vaporize directly behind the steam condensation front or at a location far behind the front in the steam zone. The conditions that delineate which situation would be found have been outlined in Yuan and Udell (1993). In general, compounds with large vapor pressures or low residual saturations would be expected to be vaporized at a rate that is high enough that the hydrocarbon distillation wave velocity would be greater than the steam condensation front velocity. As such, the hydrocarbon liquid would appear to be displaced by the steam condensation front since any hydrocarbon liquid left in the steam zone would vaporize, be convected to the steam condensation front, co-condense, and coalesce with any other hydrocarbon liquid in the vicinity. For hydrocarbon compounds with lower vapor pressures and/or high residual saturations, the distillation front would move though the soil with a velocity less than that of the steam condensation front. In that case, hydrocarbon liquids will remain in the steam zone and will be recovered through continuing steam distillation processes. Figure 3 from Yuan and Udell (1993) shows the various evaporation wave velocities of example liquid hydrocarbons as functions of the residual hydrocarbon saturations. Also shown in this figure as the horizontal dotted lines are two typical steam condensation front velocities. The first situation of an apparent complete removal of the contaminant near the condensation front corresponds to conditions above the horizontal lines in figure 3. This condition would be typical of

the removal of compounds such as toluene and those in gasoline which are relatively volatile. Steam injection into a liquid gasoline or toluene contaminated sand forms a liquid hydrocarbon bank ahead of the steam condensation front (Hunt, Sitar and Udell, 1988). However, steam injection was not observed to develop an mobile liquid hydrocarbon bank during steam injection experiments with liquid diesel (Basel, 1992). Since diesel hydrocarbons are typically of lower vapor pressure than decane, one would not expect a growing bank of diesel to appear ahead of the steam front according to theory represented in figure 3.

For non-aqueous phase contaminants with boiling points lower than that of steam at pressures near atmospheric, vaporization will occur in the rapidly decreasing temperature zone ahead of the steam condensation front (see Figure 2). The resultant contaminant vapor would then migrate in a direction determined by a combination of buoyancy and pressure forces, and the local temperature field. In one dimension, the low boiling point liquid will be mobilized ahead of the steam condensation front in spite of capillary forces which would otherwise trap the second phase liquid. As evidenced by the experimental observation of second phase contaminants flowing from the exit in non-emulsion form during the experiments reported by Hunt, Sitar and Udell (1988), it is expected that the contaminant vapor either condenses upon the second phase liquid or forms emulsions which coalesce to the second phase liquid bank. Without doubt, pure separate liquid phase contaminants with boiling points less than that of water will be completely removed from the steam zone except for the small amount which is adsorbed to solid surfaces or is dissolved in liquid water which will be present in the steam zone.

Desorption Of Contaminants

When fluids containing a contaminant come into contact with a solid such as a porous matrix, there is a tendency for a fraction of the contaminant to adsorb onto the solid surface. While the mass of adsorbed contaminant is determined by the solid specific surface area, the fraction of organic

carbon and the partitioning of the contaminant in the various fluid phases, it is also a strong function of temperature. Adsorption arises because of intermolecular forces between the contaminant and the solid surface. In soil systems the attractive forces between organic carbon and organic contaminants are particularly large. For an isothermal system, an increase in pressure (or fugacity) will result in an increase in the contaminant adsorption as predicted by a Langmuir adsorption isotherm. Yet, for this adsorption to occur, a considerable amount of heat must be released which is called the latent heat of adsorption. Likewise, for desorption to occur, energy must be supplied to the system. The energy necessary for desorption to occur in contaminated soils can be provided by steam condensation. Also, an increase in the temperature of the contaminated soil increases the intermolecular forces required for a surface to hold a molecule. Thus, the adsorbed mass of contaminant will decrease for an increase in temperature for a fixed fluid composition. As an example, the use of low pressure steam to regenerate activated carbon used in solvent recovery systems has been common in industry for decades (Scheflan and Jacobs, 1953).

In the context of the steam injection/vacuum extraction process, desorption of volatile compounds is expected to occur in the steam zone in a wave-like manner analogous to that of second phase contaminant evaporation. Also, the desorption of compounds from solid surfaces to the aqueous phase in the region ahead of the condensation front is expected due to the increase in temperature as the steam zone approaches. However, high contaminant concentrations near the steam and contaminant condensation front may lead to re-adsorption, depending on the adsorption characteristics of the contaminants and soil at steam temperatures.

Boiling Of Interstitial Water

The thermodynamic system consisting of steam, water, semi-volatile contaminant, and porous matrix found within the steam zone is complex and unusual. Because of capillary forces stemming from the radius of curvature of the water-vapor interface, the water is in a stable superheated state

in equilibrium with a slightly superheated vapor (Udell, 1983). This situation produces an effective liquid to vapor phase change mechanism where a decrease in the local vapor pressure will promote distributed pore scale evaporation of the interstitial water at a rate determined primarily by the rate of de-pressurization and heat transfer from adjacent solids. From energy and mass balances on an adiabatic control volume containing steam, water and a porous matrix, it is evident that the removal of the enthalpy of a given mass of steam , will require a corresponding decrease of the system internal energy as well as a decrease in the interstitial water mass. The decrease in the porous matrix internal energy provides the necessary heat for the vaporization of the liquid water. With continued steam withdrawal, the system temperature will continue to drop until the liquid water content is reduced to zero. The significance of this effect is that the vacuum withdrawal of steam from the steam zone can produce a vapor flux from microscopic and macroscopic regions that would not be otherwise contacted by flowing steam. This mechanism can be brought to bear in a field process by simply stopping steam injection to a contaminated region while maintaining a vacuum withdrawal of the vapor phase and continuing liquid pumping. Reduction of the water content to zero would require high steam pressures and minimal liquid water re-infiltration. One-dimensional data supporting this theory was presented previously (Udell and Stewart, 1992). Two-dimensional and field data showing the higher recovery rates by this mechanism is presented in the following sections.

Two-Dimensional Studies

Two-dimensional steam injection experiments have been performed with a 5 cm thick sand pack, a meter in height and a meter in width, with visualization capabilities. The gravitational orientation of the experiments allowed visual studies of fluid distributions that might be expected under field conditions as well as the effects of gravity on the movement of the steam condensation front. These studies have shown that the conclusions drawn from the one-dimensional studies also

pertain to the recovery of non-aqueous phase contaminants from much more complex situations. Specifically, the differences in the distillation wave velocities for various compounds predicted by theory (Yuan, 1991 and Yuan and Udell, 1993) has been visually observed in the two-dimensional experiment. Also, the limitation of steam channel lengths due to heat losses to adjacent material has been confirmed (Basel, 1991, Basel and Udell, 1991). However, other important mechanisms influence the movement of the contaminants in a gravity field. Most important of these effects is the phenomenon termed steam over-ride. If the applied horizontal steam pressure gradient is much less than the hydrostatic pressure gradient, then the steam has been observed to move to the top of the confined sand pack (Basel and Udell, 1989). If the ratio of the horizontal pressure gradient to the hydrostatic pressure gradient is about one, gravitation control of the steam zone is obtained. For this ratio equal to one, the angle of the steam condensation front interface in a homogeneous medium been predicted and observed to be 45° from horizontal. For higher steam pressure gradients, the steam front becomes more vertical. Layered media has been found to give additional gravitational stability to the steam condensation front.

The removal of second phase liquid contaminants from the two-dimensional sand packs was also studied using this apparatus. Figure 4 shows the displacement of o-xylene in response to the moving steam front. The conditions of this experiment are scaled to represent a spill at 3.5 m depth, with 10 m spacing between wells. The displacement required about 350 pore volumes of steam to remove the xylene from the sand pack. In this case, the steam appeared to mobilize the xylene as a free product bank ahead of the steam condensation front. Different results were obtained using lower volatility diesel fuel. A layered sand pack was used in this experiment to examine the effects of larger scale heterogeneities on the movement of steam and the contaminant liquid. Figure 5 shows the initial location of the diesel pool, the movement of the diesel as a mobile separate phase and the region where residual diesel liquid was observed after steam breakthrough. As indicated in these figures, there was not significant physical displacement of the diesel by the steam condensation front. While there was some initial steam displacement of the free

product diesel, the volume of the mobile pool decreased with time and residual hydrocarbon liquids were observed in all regions that had contained liquid diesel. These results are in agreement with the theory of Yuan and Udell (1993). The higher volatility of the xylene would have allowed a velocity of the xylene vaporization wave to be greater than the steam condensation front velocity, providing the appearance of complete displacement. The evaporation wave velocities of components such as those found in diesel fuel are slower than the steam condensation front velocity, thus their removal by steam injection is then dominated by steam distillation in the steam zone. In such a situation, one would expect multiple evaporation wave velocities: one for each component (Yuan, 1991). This is born out in the gas chromatographic analysis of effluent liquids and the residual diesel left in the sand taken from the location indicated in figure 5. Figures 6a - 6c show the chromatograms of two effluent samples and a residual sand sample. It is clear from examination of these chromatograms that the evaporation wave velocities of the more volatile compounds (shorter retention times) were fast enough to be removed in the time-frame of the experiment. The less volatile (longer retention times) components remain until the evaporation wave of that compound passes each location.

Also of interest in these series of studies was the observation of the enhancement of the mass transfer of the contaminant from the low permeability regions during the de-pressurization mode of operation. In this mode, the porous media becomes an *in situ* steam generator, producing an convective flow of steam from the low permeability regions to the higher permeability regions, thus enhancing the mass transfer rates. Figure 7 shows the effluent concentrations of a four component pseudo-gasoline mixture of pentane, hexane, toluene, and decane during both steam injection and vacuum de-pressurization modes of operation. While high recovery rates were observed just before steam break-through indicating displacement similar to that of pure xylene, the removal rates of the hydrocarbon mixture during the vacuum mode were of comparable magnitude.

Field Studies

Two field studies have been operated to examine the effectiveness of steam injection to recover contaminants from spill sites. The first site demonstration, Solvent Service, Inc., was a pilot study of small dimensions with multiple contaminants found in the vadose zone. The second field demonstration, Lawrence Livermore National Laboratories, was a gasoline spill with second phase liquid contaminants found both above and below the water table. The gasoline was found to extend from about 17 m to 45 m from the surface. The general process schematic for the process used at both sites is shown in Figure 8.

<u>Solvent Service, Inc., San Jose, California,</u>

The site chosen for the study had been used as a solvent recycling and acid treatment facility since 1973. Soil contamination at the site resulted from leaking underground storage tanks and surface spills associated with the handling of these industrial wastes. Twenty organic volatile compounds and six non-volatile compounds have been identified at the site. Fourteen of the organic compounds have been detected in concentrations exceeding 1.5 ppm. The principal contaminants of the soil are xylenes, ethylbenzene, 1,2-dichlorobenzene, 1,1,1-trichloroethane and acetone which, along with trichloroethene and tetrachloroethene, occur with maximum concentrations greater than 500 ppm.

A clay barrier was located approximately twenty feet below the surface which inhibited the further vertical migration of the contaminants. Perched water was found in a one foot zone on top of the clay layer. The soil was unsaturated above the perched water. In characterizing the extent of soil contamination, the complications associated with mixtures were apparent. High concentrations of acetone were found throughout the site which is not surprising given its high volatility and complete miscibility in water. Most of the other contaminants at this site were miscible or highly

soluble in acetone. Thus, the acetone provided a mechanism for contaminants with low water solubilities and mobilities to migrate with the water.

The location of the pilot study was in the region of highest contaminant concentrations. Total contaminant concentrations were 10,000 ppm in some locations. The pattern of injection and recovery wells used for the pilot study was selected as a prototype for a design to remediate a spill site similar to the LLNL gas pad. The system consisted of a central recovery well surrounded by six injection wells evenly spaced on a 3.1 m (10 ft.) diameter circle. The injection wells were drilled to 6 m (19 ft), but completed over only the bottom three feet. The recovery well was completed throughout and extended into the clay layer. Liquids were removed from the recovery well via a jack pump and vapors were drawn out through application of sub-atmospheric pressure provided by a vacuum pump placed on an extraction line downstream of a condenser. Also, 12 temperature observation wells were placed inside the pattern, 3 on the edge, and 2 outside the pattern.

After 140 hours of steam injection and vacuum extraction, nearly 400 kg of contaminant was recovered, accounting for over 90% of the original contaminant mass. Post steam injection soil sampling showed low levels (> ppm total) of contaminants in the high permeability zones which had ample steam contact. However, high levels (near initial values) of some contaminants (particularly high water solubility compounds) were found within the lower permeability zones. Given the short process operation time, such results were expected. It should also be mentioned that the recovery rates at the end of the 140 hours remained high. Further details of this project can be found elsewhere (Udell and Stewart, 1989).

Injection cycling at the end of the pilot did produce contaminant vapors in higher concentrations in the gas stream than those measured during steady steam injection. The effectiveness of this phase of the steam injection/vacuum extraction process for recovering contaminants from the low

permeability regions could not be adequately tested at this site without re-contaminating the steamed region by drawing in contaminants from outside the test pattern.

Lawrence Livermore National Laboratory, Livermore, California

In a more recent study, steam was injected both above and below the water-table at Lawrence Livermore National Laboratory in an effort to cleanup gasoline-contaminated soil within water-bearing zones. This project is referred to as Dynamic Underground Stripping. The site plan and hydogeologic section are shown in Figures 9 and 10, respectively. The subsurface geology was of alluvial origin, with layers of high permeability interspersed with clays and clayey silts. The horizontal correlation of the high permeability layers was moderate except for a thick gravel layer found below the water table from about 35 m (140 ft.) to 42 m (150 ft.). This gravel layer was found in each well surveyed. The gasoline was detected as a second phase in an area about 50 m (150 ft.) in radius as shown in Figure 9. The vertical distribution ranged from 17 m (50 ft) to about 45 m (137 ft.) in depth as shown in Figure 10, with significant spreading due to major ground water elevation fluctuations. Indeed, separate phase gasoline was found in the deep water-bearing zone nearly 8 m below the water table as shown. This situation rendered others technologies such as ambient temperature vacuum extraction to be impracticable, and groundwater extraction to be time-prohibitive. There were two major flow zones at this site: the deep gravel layer and an upper unsaturated zone consisting of intermingled sands, silts, clays and gravels. A contaminated clay layer of variable thickness separated the two permeable zones.

Six injection wells were placed around the perimeter of the area contaminated by separate phase gasoline; three recovery wells were installed near the center of the plume as shown in the site plan of Figure 9. The injection wells were constructed to allow separate steam injection into the upper and/or lower permeable regions. The recovery wells were completed over the entire height of the

contaminated zone. Also shown in Figure 9 are the placement of the 11 temperature observation wells.

During the first steam pass, steam was injected first into the lower gravel layer below the water table for two weeks. Steam broke through at the recovery wells about 10 days after injecting steam. After the first two weeks, steam injection into the upper zone while continuing steam injection into the lower zone at a lower rate. This lower rate did not provide sufficient energy into the gravel layer below the water table to maintain the steam zone. Thus the steam flow rate into the recovery wells dropped to zero until steam broke through to the recovery wells in the upper zone on the 23rd day from the initiation of steam injection. From day 21 to day 30, steam was injected only into the upper zone. From day 30 to day 37, steam was injected only into the lower zone. Steam broke-through again into the lower zone on day 32. Steam injection and fluid extraction ceased at the end of day 37 for a period of 3 months while higher capacity treatment equipment was installed. Steam injection resumed for a second pass on 6/2/93 after 9 days of groundwater extraction and vacuum pumping. The steam injection schedule was periodic with periods of steam pressurization and de-pressurization. Steam was injected a total of 21 days during this 46 days of gas and groundwater extraction. Vacuum extraction and groundwater pumping resumed in October and continued for a period of 70 days. Electrical heating occurred during November for a period of 10 days. No steam was injected during this final 70 day phase.

Temperature logs in each of the 11 temperature monitoring wells were obtained daily during the first two phases of this demonstration. Sample temperature profiles inside the ring of injection wells at the end of the first and second pass of steam injection are shown in Figure 11. For reference, the lithology log is superimposed to show the correlation between the geologic features and the development of the temperature field. Electrical heating prior to steam injection raised temperatures by up to 50° C, and seemed to preferentially heat those zones that were not readily heated by steam (TEP - 7). While the steam initially entered the highest permeability zones during

the first pass, conductive heating brought the smaller lower permeability zones to steam temperatures by the end of the second pass. Uniform temperatures in the target zones were observed in TEP - 9 and TEP- 10 by the end of the second pass. However the lower permeability zone separating the two steam zones near TEP - 7 and TEP - 8 had not yet reached steam temperature by the end of the second pass. An interesting detail seem in each of the plots is the effect of groundwater pumping on the temperature profiles in the lower steam zone. Since the energy injection rate into the lower zone was less in the second pass than in the first pass, and the pumping rates were somewhat higher, convective cooling of the lower steam zone occurred due to the infiltration of cold water from unheated zones.

The recovery rates of gasoline are shown as a function of time in Figures 12, 13 and 15. The process was operated continuously during three different intervals, with system upgrades and additional field work performed in between during the down-time. During the 1st pass (figure 12), increases in recovery rates were observed in solution, in the gas phase, and as a separate phase liquid within the first few days of steam injection with the highest rate occurring on the day of steam breakthrough into the lower interval of the extraction wells (2/15/93 and 3/3/93). Otherwise, gasoline recovery rates were limited by the use of the regenerated carbon gas treatment system with a capacity of less than 50 gallons gasoline per day. A total of approximately 1700 gallons of gasoline was recovered during the first phase. However, direct measurements of the volumes of the liquid gasoline removed from the condenser could not be made. Therefore those amounts are not shown in figure 12, except as a portion of the liquid imprecisely measured in the liquid megatorr which included the pumped free product. While a greater amount of displaced free product was expected before steam break-through in either the upper or lower zones, the recoveries were restricted by the limitations on liquid pumping rates imposed by the liquid treatment system and the intrinsic difficulty of capturing a free product bank with the two liquid pumping wells. Higher gas and liquid handling capacities in the surface equipment could have allowed increased

recovery rates. After five weeks of operation, the system was shut down to install improved liquid gasoline measuring systems and higher capacity fluid handling equipment.

The recovery rates observed during the second pass were much higher as shown in Figure 13. The increased rates were due to higher capacity gas and water treatment systems, as well as the increased subsurface temperatures and cyclic steam enhancement. The recovery rates were highest before steam injection began. Thereafter, periodic peaks in the recovery rates were measured corresponding to times when steam injection ceased and depressurization began. A total of 4900 gallons of gasoline was recovered during the second pass. The 2nd pass was terminated due to permitting restrictions on the boiler while recovery rates remained high and may have continued with additional cycles of steam injection. During the next 80 days, soil samples were collected, the steam boiler was taken from the site, and additional electrical heating wells were installed. The treatment system was shut down during this period.

The soil concentrations found after the 2nd pass are shown in Figure 14. In general, gasoline was effectively removed from the hot steam-bearing zones and concentrations were significantly reduced in the low permeability zone separating the upper and lower permeable units. An estimate of 750 gallons of gasoline remaining in the soil after the end of the second pass was made from the soil concentrations shown in figure 14.

The recovery rates during the final phase are shown in Figure 15. While significant rates of recovery were measured during the beginning of pumping, the rates fell with time, and the magnitudes were much less than those observed during the second pass. Some improvement in the recovery rates were achieved by converting upper zone injection wells into vapor recovery well. However, little could be done to increase recovery rates during the final few days of operation: including electrical heating. Regardless, an additional 1000 gallons of gasoline were recovered in

this final phase before the recovery rates dropped to small values. The cumulative total of gasoline removed was 7600 gallons at the end of operation.

Subsequent gas and water sampling is showing decreasing concentrations of gasoline components with time, implying that there is no separate phase gasoline remaining at this site. Ethybenzene, toluene, and xylene concentrations in the water have dropped to below MCL. Benzene concentrations continue to decrease. Hydrocarbon-degrading biological activity was found in the zones subjected to steam temperatures, indicating that the application of steam did not leave the site sterile. The culture make-up however, has been dramatically altered. It is expected that no further treatment will be required. Details of all aspects of the Livermore field demonstration can be found in reports to follow (Newmark, ed., 1994).

Conclusions

The results of several years of experimental, theoretical, and field research have shown the applicability of steam injection and fluid extraction to the *in situ* cleanup of second liquid phase contaminants found both above and below the water-table. The primary mechanisms responsible for the effectiveness of steam injection and fluid pumping are: the acceleration of the vaporization of volatile and semi-volatile compounds, the displacement of the pore fluids by the steam condensation front, desorption of contaminant adsorbed to the solids, and the enhanced vaporization of contaminants in the low permeability zones during the cyclic steam injection operation. With proper design and operation, this method of soil and ground water remediation is found in practice to be rapid, robust, and relatively predictable.

Acknowledgments

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Yuan, Z-. G., and Udell, K. S. 1993, "Steam Distillation of a Single Component Hydrocarbon Liquids in Porous Media," *International Journal of Heat and Mass Transfer*, Vol 36, No. 4, pp.887-897.
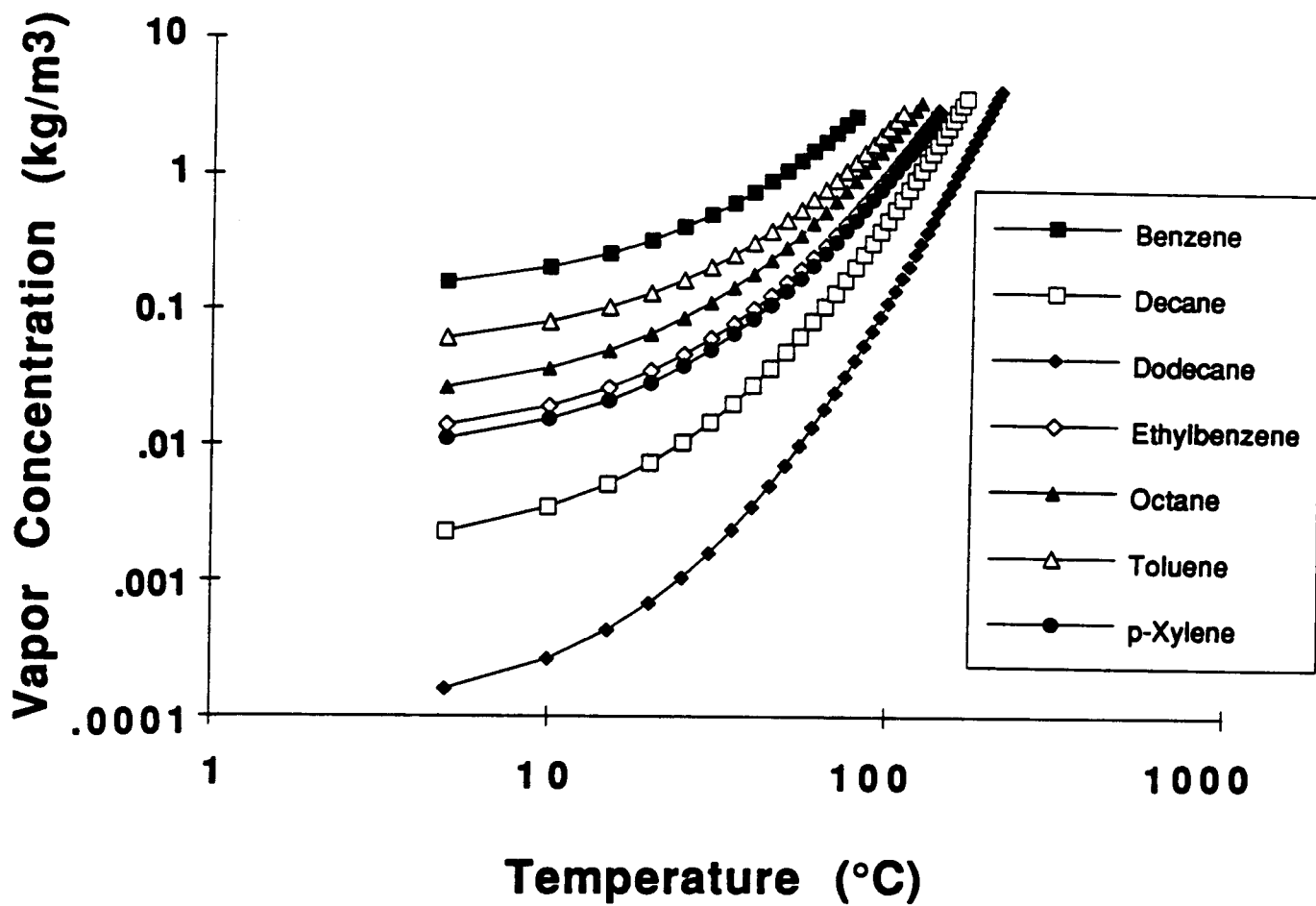
Figure 1   Vapor concentrations of various hydrocarbons versus temperature.
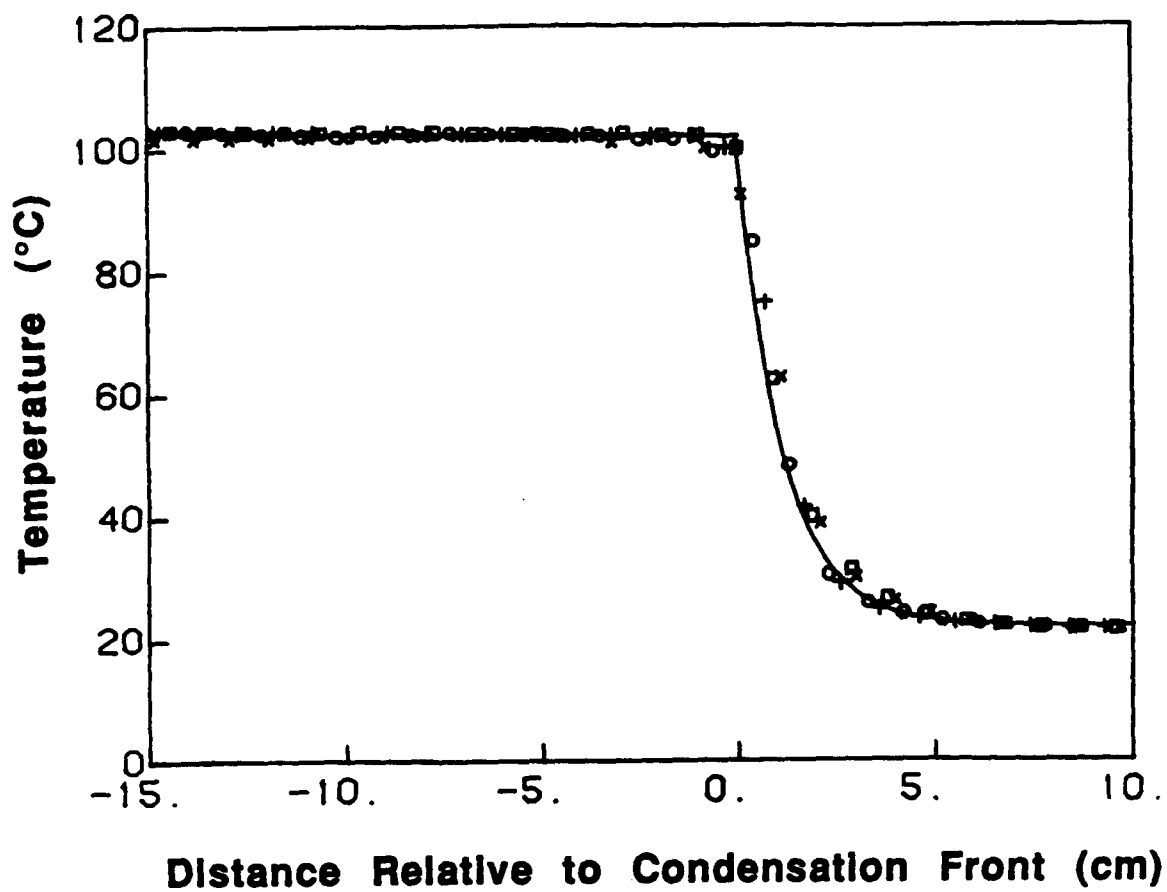
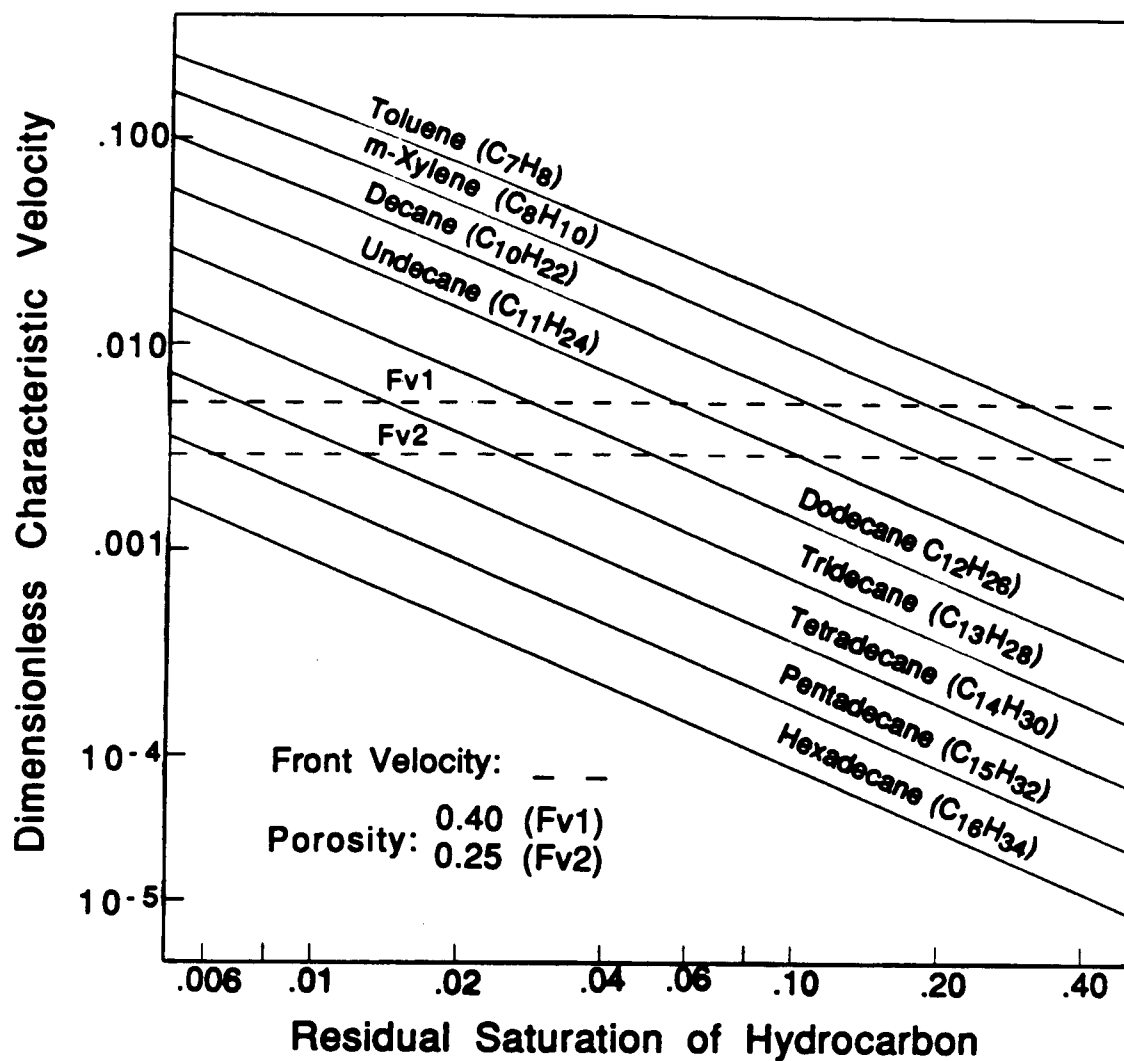Figure 2   Temperature profile near the steam condensation front.

Figure 3   Velocities of evaporation waves of various hydrocarbons versus hydrocarbon content in the soil. Also shown are the condensation front velocities for two different porosities. If the velocity of the evaporation wave is greater than the steam condensation front velocity, then the hydrocarbon will appear to be completely displaced by the steam.
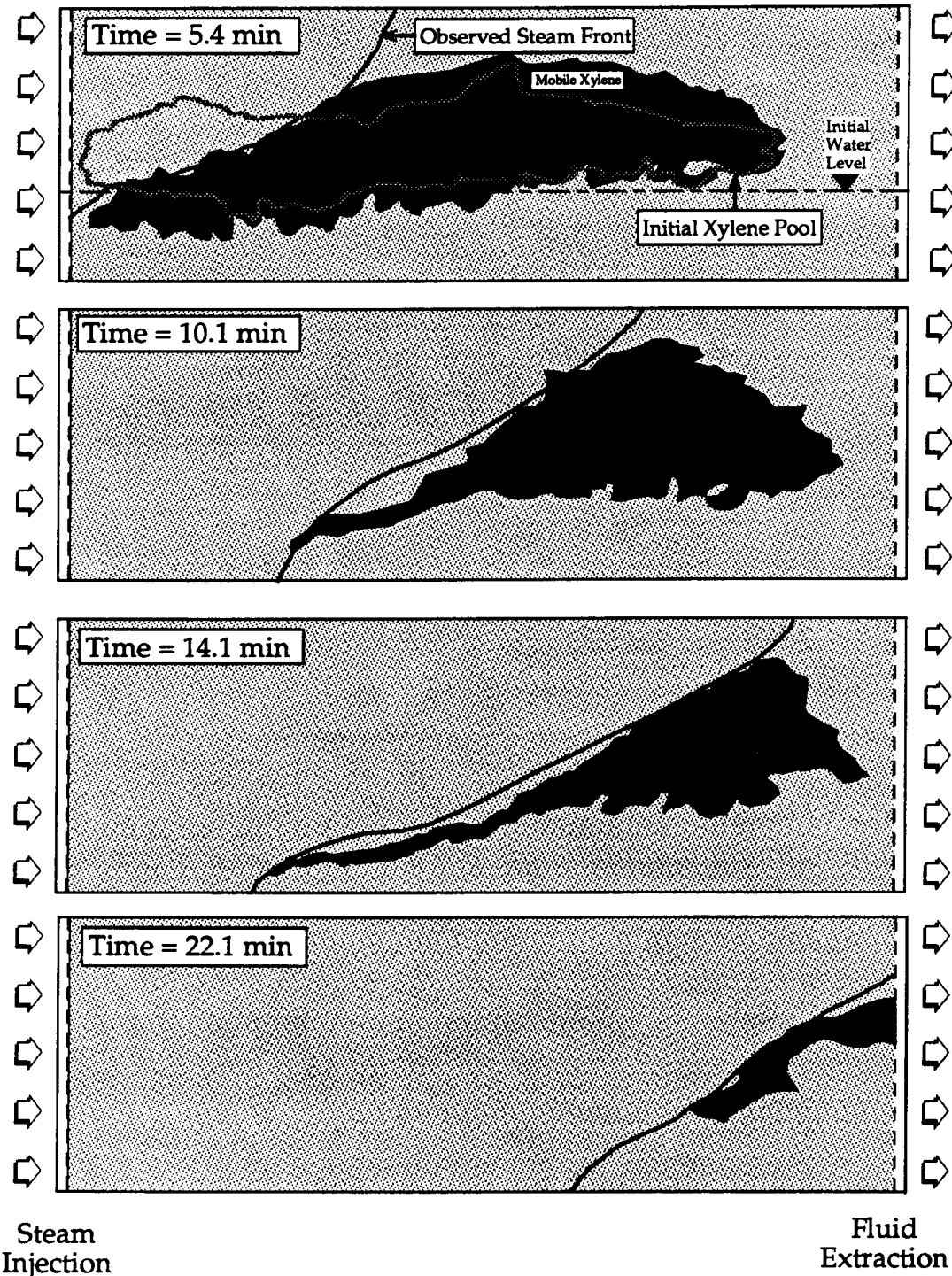
Figure 4   Displacement of a pool of xylene floating on the water table (from Basel, 1991).
As the steam front reaches the edge of the pool of xylene (5.4 min), the xylene begins
to vaporize and be displaced by the steam. After 10 minutes of injection,
the pool of xylene begins to mound on the bank of water being displaced by the steam.
After 18 minutes, the pool of xylene has been displaced to the exit port and is being
recovered as free product. Thirty minutes was required to completely recover the pool.
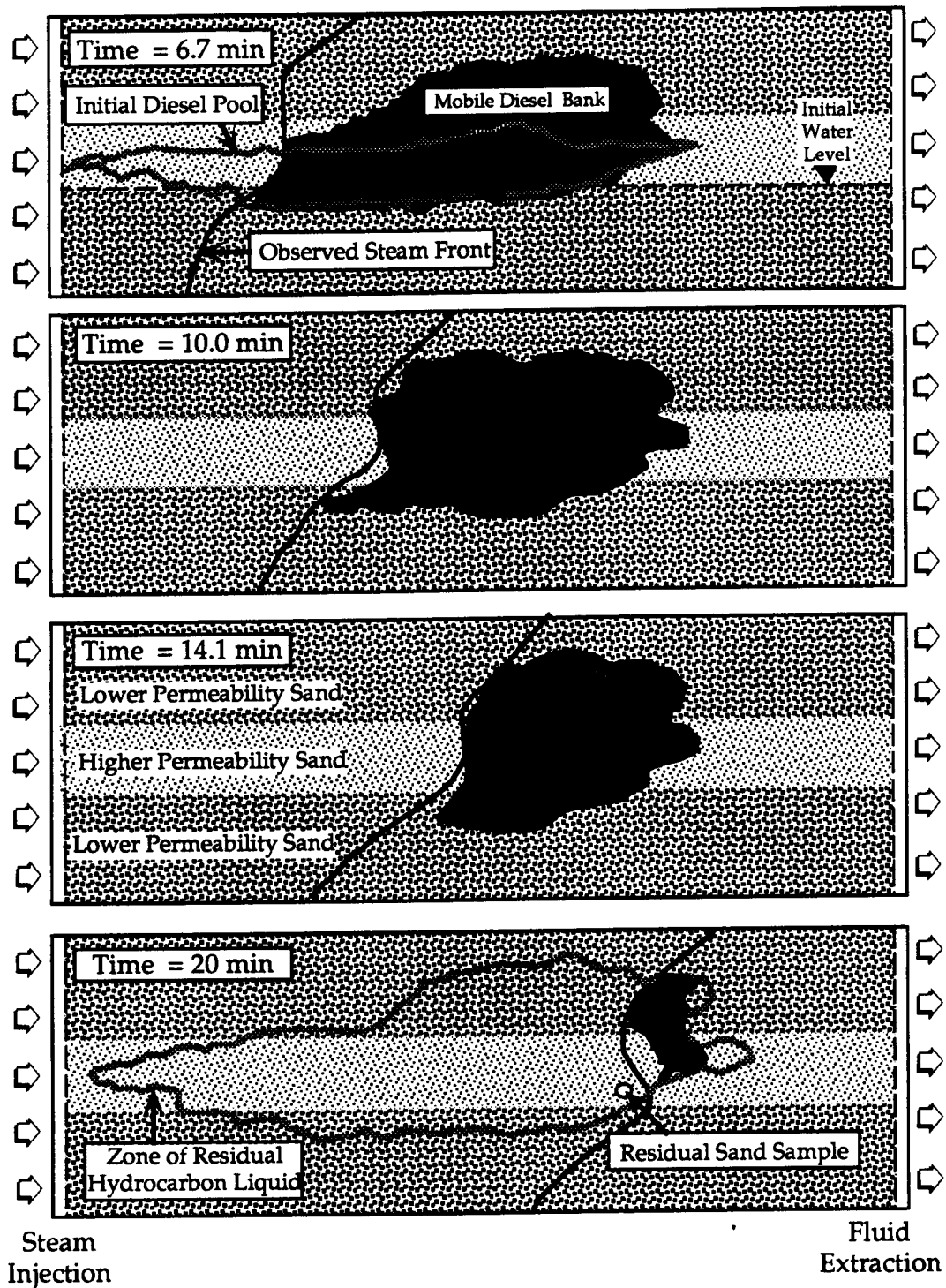
Figure 5   Displacement of a pool of diesel floating on the water table in a heterogeneous sand pack (from Basel, 1991). While there was some initial steam displacement of the free product diesel, the volume of the mobile pool decreased with time and residual hydrocarbon liquids were observed in all regions that had contained liquid diesel . Due to the low volatility of diesel components, the appearance of a co-condensed hydrocarbon bank at, and ahead of, the steam condensation front would not be expected. Diesel compounds were recovered predominantly in the vapor phase by steam distillation.

A. Effluent sample during
1ˢᵗ vacuum extraction.

A

Reference
peak

B. Effluent sample during
2ⁿᵈ steam injection.

B

Reference
peak
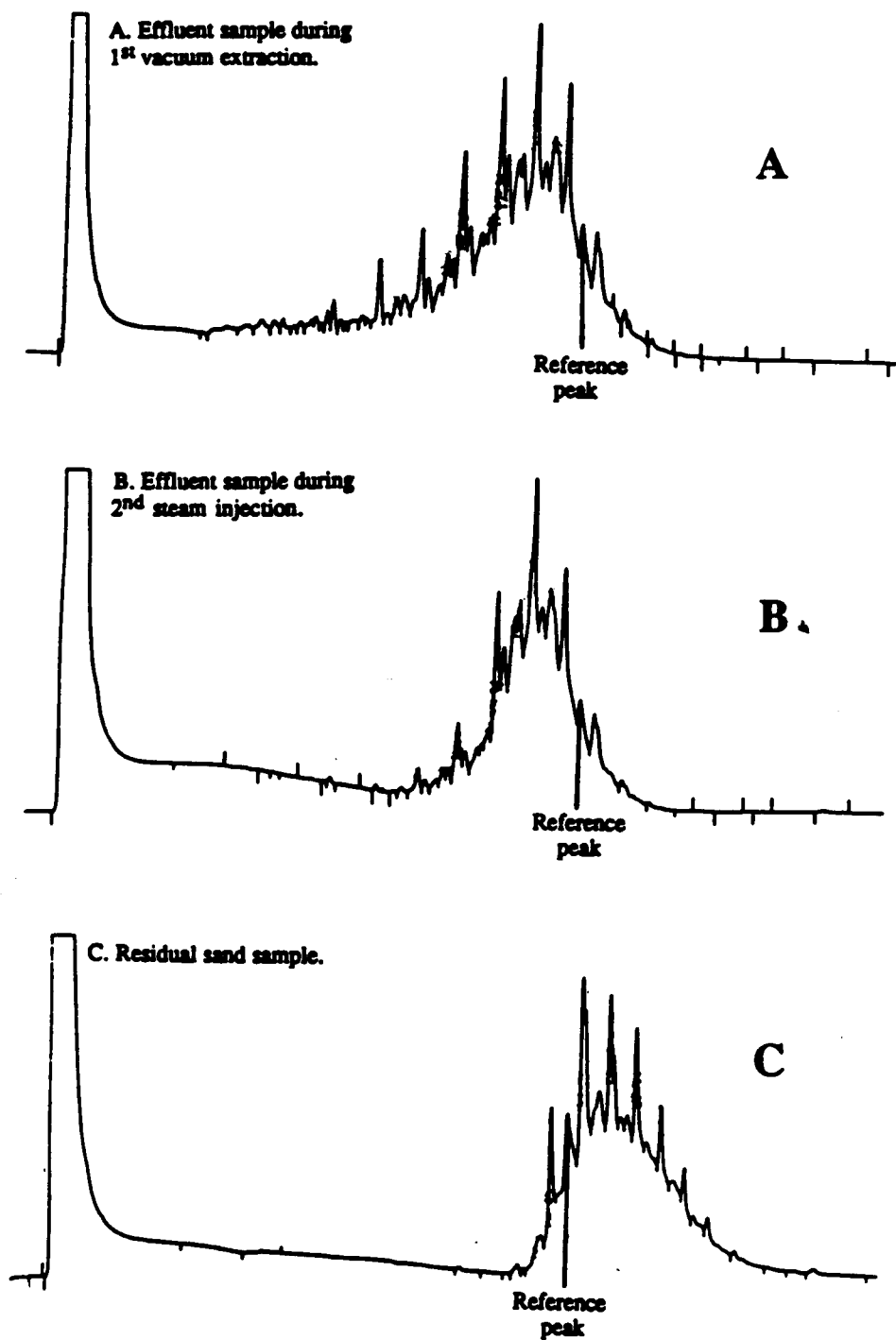
C. Residual sand sample.

C

Reference
peak

Figure 6   Gas chromatograms of diesel removed in the vapor phase (A and B) and of
the residual remaining after steam contact (C). Evidence of preferential
steam distillation of the more volatile diesel components is shown (from
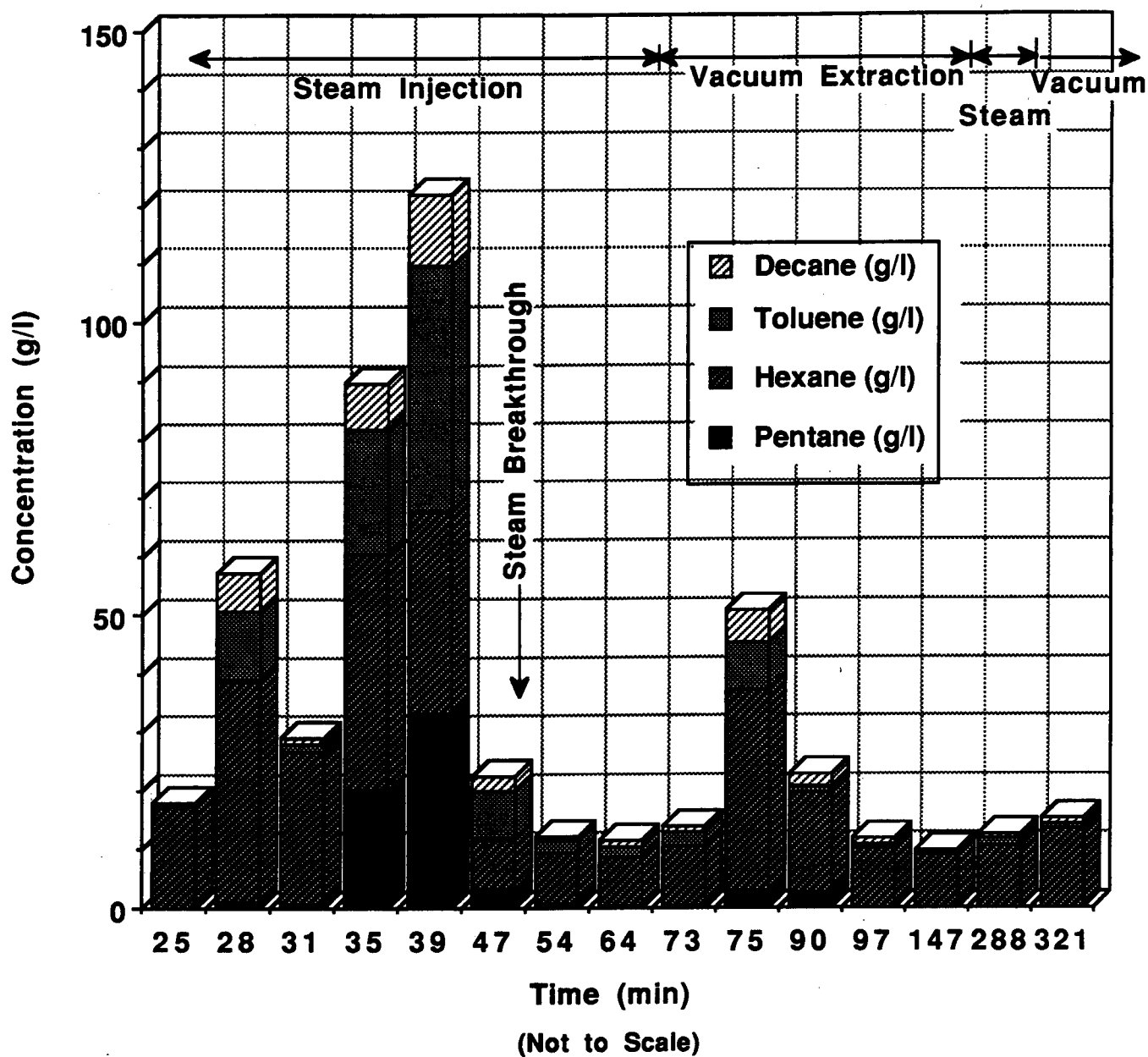Basel, 1991).

Figure 7   Effluent concentrations of a hydrocarbon mixture of pentane, hexane, toluene and decane from a two-dimensional, heterogeneous sand pack during steam injection and vacuum de-pressurization modes of operation. The highest concentrations were observed just before steam breakthrough in each of the high permeability zones, and during the period of de-pressurization immediately after cessation of steam injection.
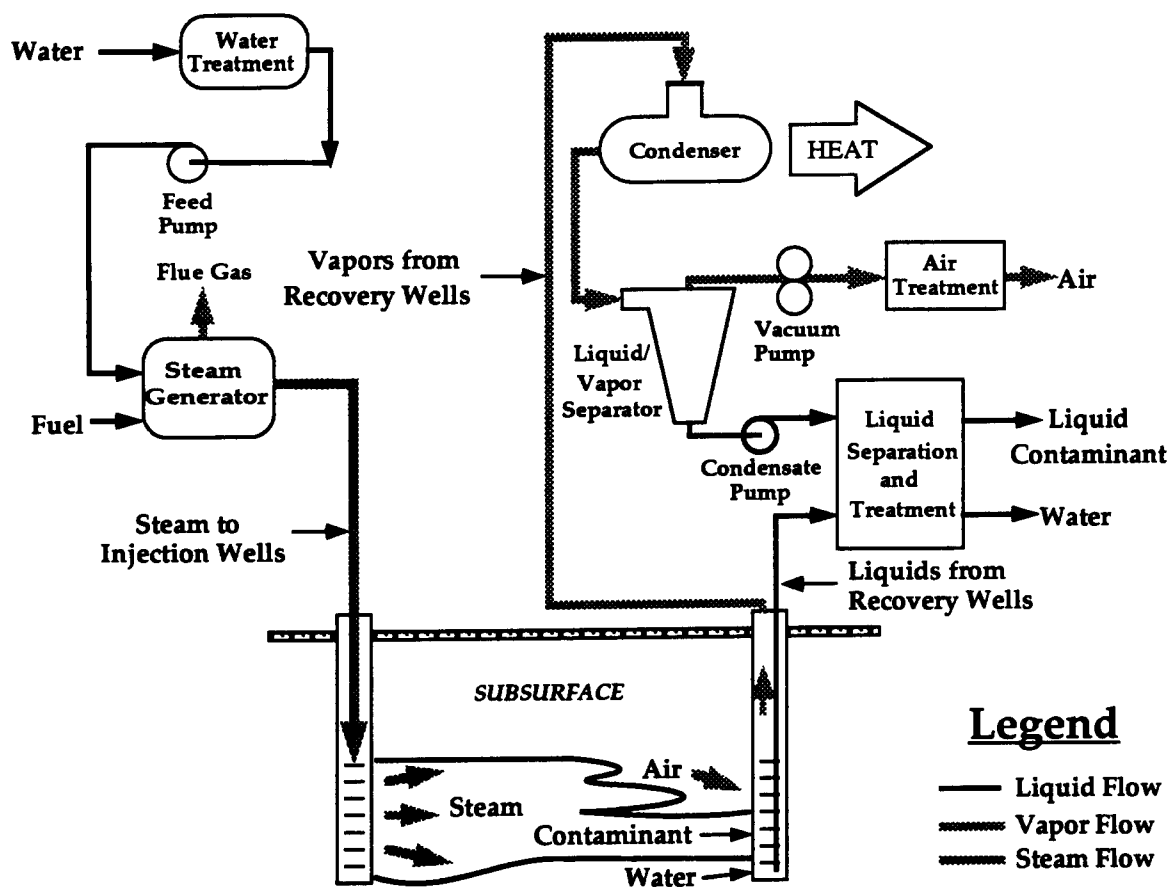
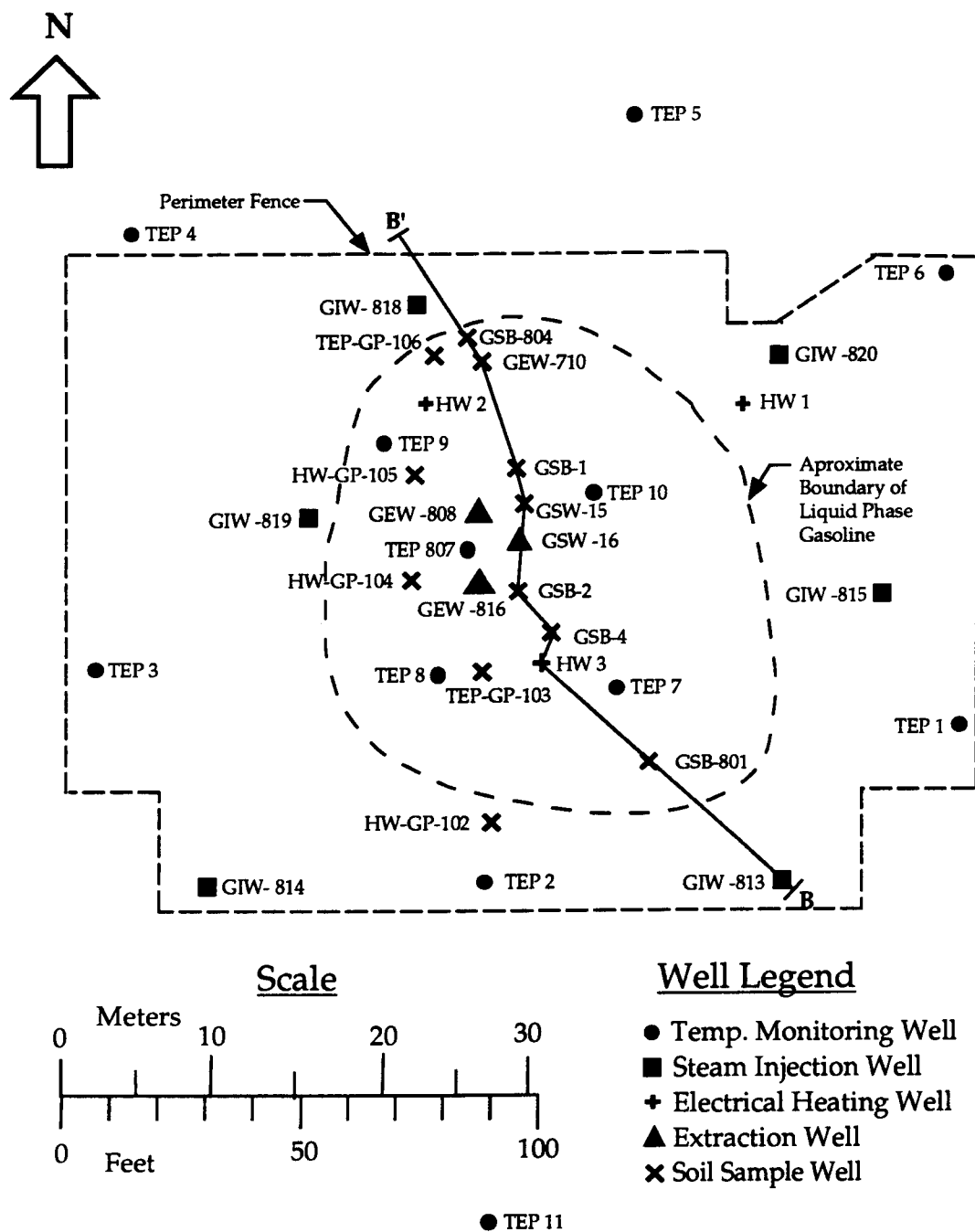Figure 8 Process schematic of steam enhanced extraction.

N

● TEP 5

Perimeter Fence

B'

● TEP 4

TEP 6 ●

GIW- 818 ■

TEP-GP-106 ✕ GSB-804
✕ GEW-710

■ GIW -820

+ HW 2

+ HW 1

● TEP 9

HW-GP-105 ✕

✕ GSB-1

Aproximate
Boundary of
Liquid Phase
Gasoline

✕ GSW-15 ● TEP 10

GIW -819 ■ GEW -808 ▲

TEP 807 ● ▲ GSW -16

HW-GP-104 ✕ ▲

✕ GSB-2

GEW -816

GIW -815 ■

✕ GSB-4

+ HW 3

TEP 8 ● ✕ ● TEP 7
TEP-GP-103

TEP 3 ●

✕ GSB-801

TEP 1 ●

HW-GP-102 ✕

■ GIW- 814

● TEP 2

GIW -813 ■
B

Scale

Meters
0   10   20   30

0   Feet   50   100

● TEP 11

Well Legend

● Temp. Monitoring Well
■ Steam Injection Well
+ Electrical Heating Well
▲ Extraction Well
✕ Soil Sample Well

Figure 9   Site plan of the LLNL demonstration project.

5-38
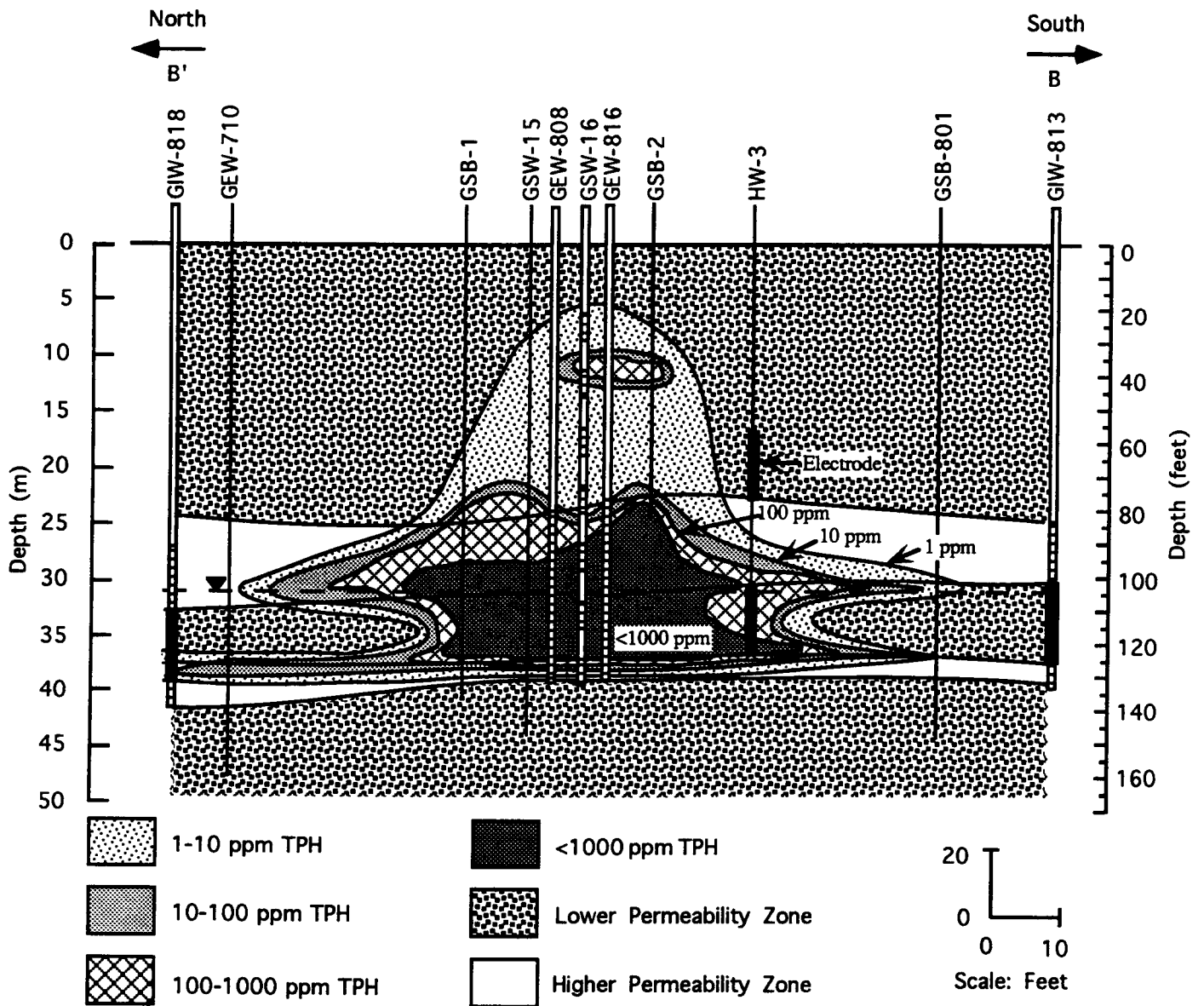
Figure 10   Simplified geologic cross-section showing approximate initial distribution
             of gasoline, the upper and lower steam zones, the injection and extraction
             well screened intervals, the electrode locations, and the water table elevation.
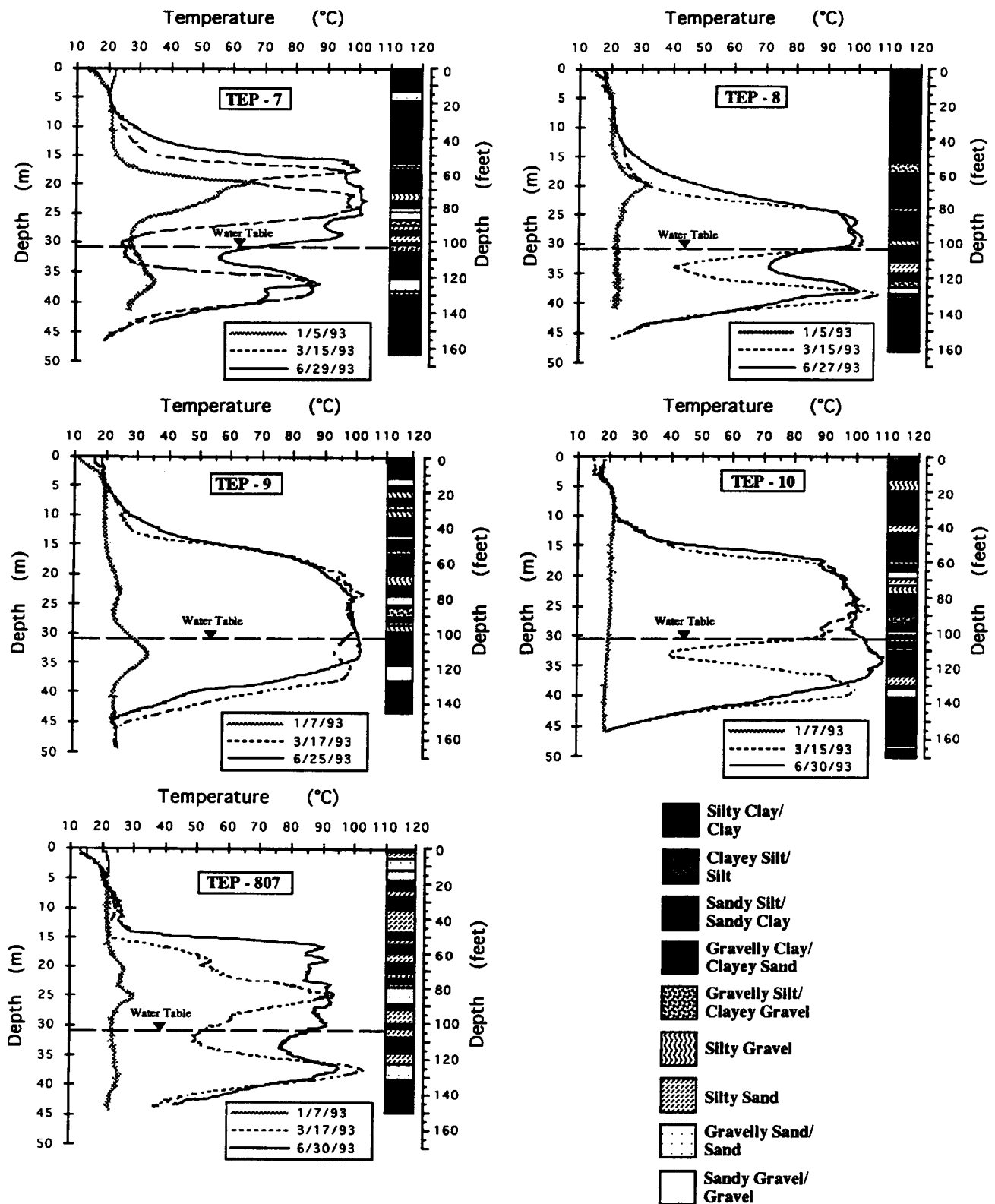
Figure 11. Temperature profiles in wells inside of steam injection ring. The gray lines are the temperature profiles near the end of electrical heating, dotted lines represent the temperature profiles near the end of the first pass, and the solid lines represent the temperature profiles near the end of the second pass. The subsurface lithologies are superimposed to show correlations between the subsurface geology and the development of the thermal field.
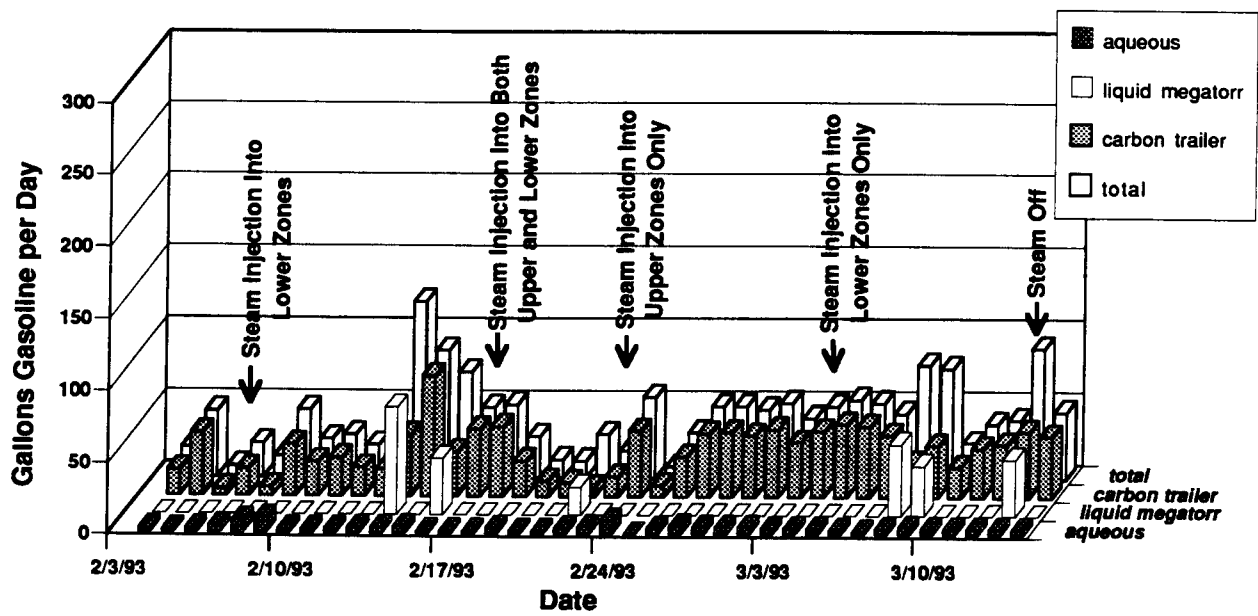
Figure 12   Recovery rates of gasoline during the first pass.
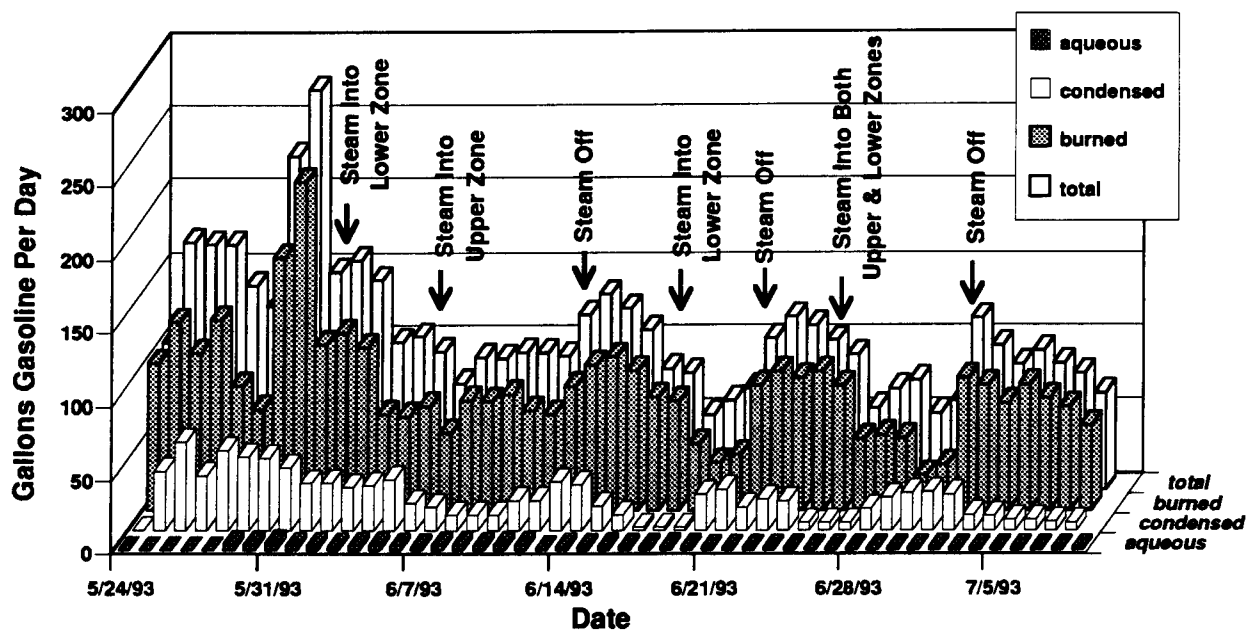
Figure 13   Recovery rates of gasoline during the second pass.
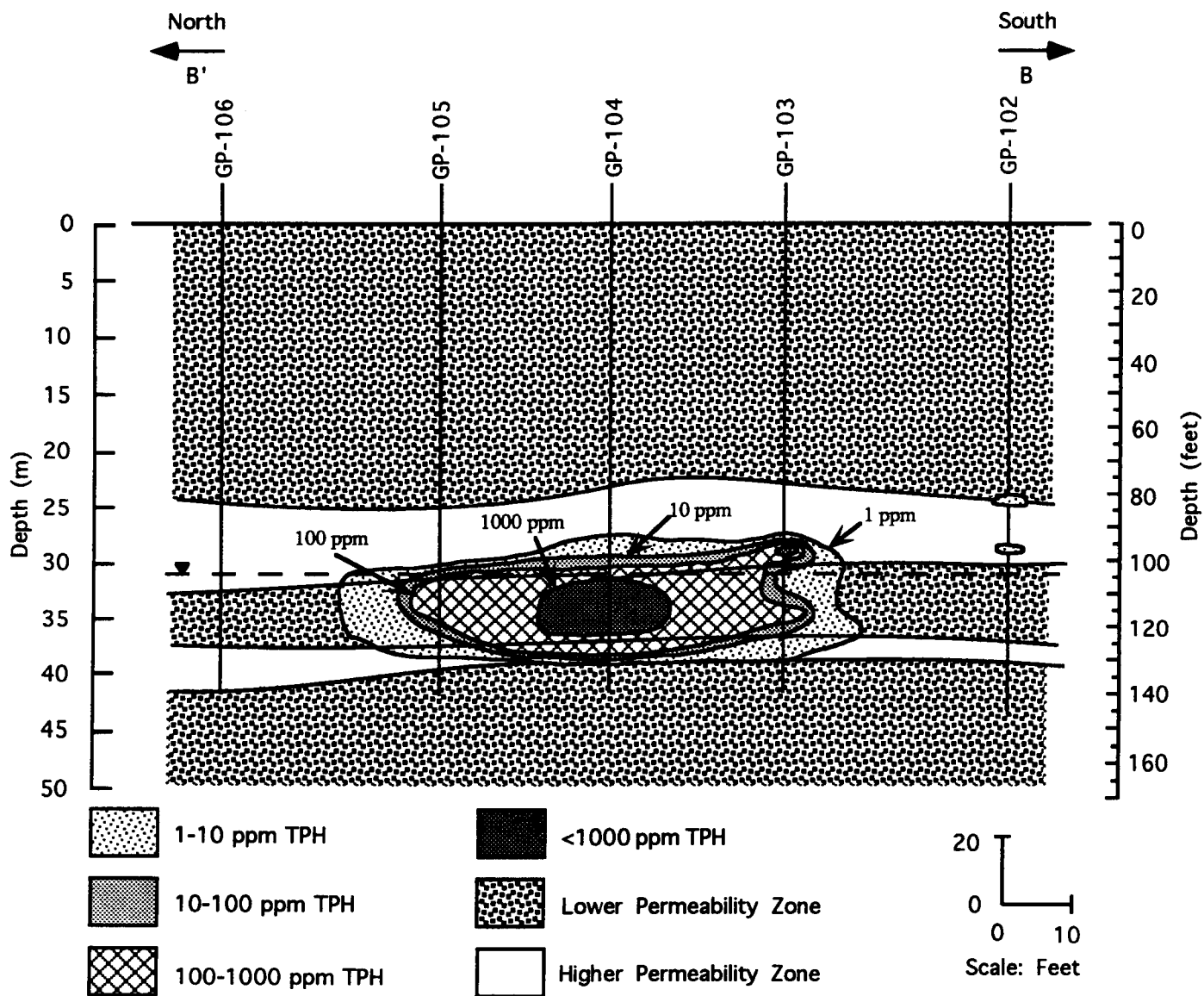
Figure 14   Simplified geologic section showing the approximate distribution
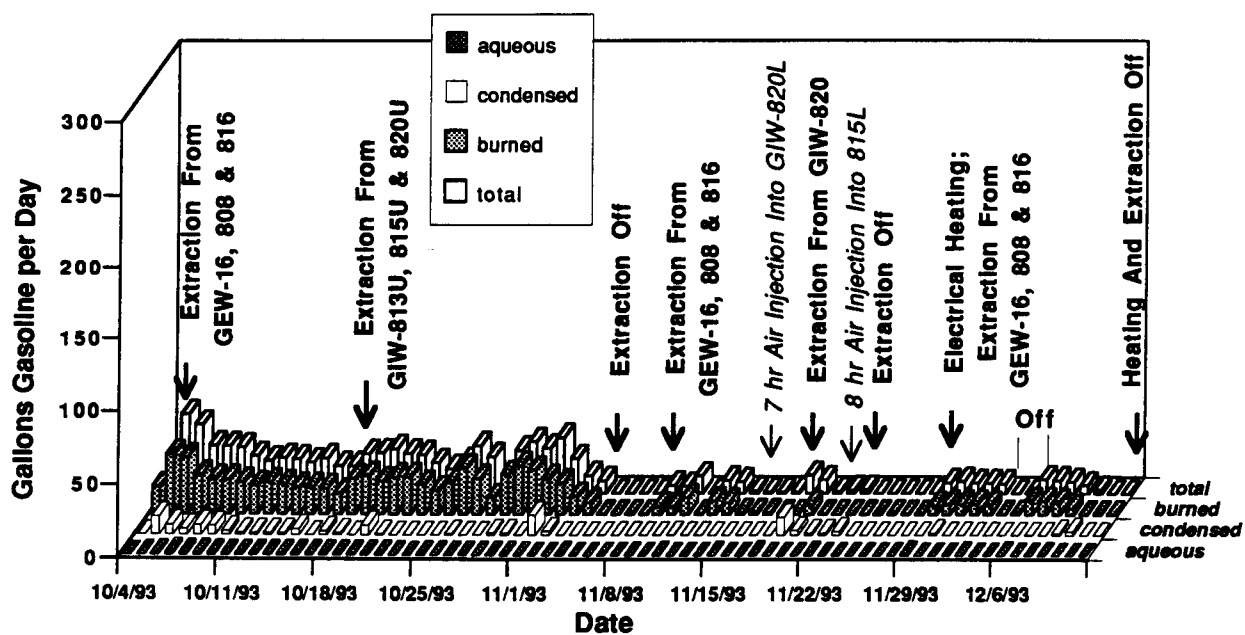   of gasoline after the second pass.

Figure 15   Recovery rates of gasoline during the final operation of the pumping system.